DEVELOPMENT OF PROCESSING TECHNIQUES FOR ADVANCED THERMAL PROTECTION MATERIALS

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Report submitted to:

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Introduction

The main effort for the period June 1, 1995 through May 31, 1996 has been in the development of materials for high temperature applications. Thermal Protection Systems (TPS) are constantly being tested and evaluated for thermal shock resistance, high temperature dimensional stability, and tolerance to environmental effects. Materials development was carried out through the use of many different instruments and methods, ranging from intensive elemental analysis to testing the physical attributes of a material. There were two main areas of focus including (1) development of coatings for carbon/carbon composites and (2) development of ultra-high temperature ceramics (UHTC). This report describes the progress made in these two areas of research during this contract period.

(1) Development of Protective Coatings for C/C Composites

The thermal and structural properties of C/C composites are ideal for many thermal protection applications. However, carbon is highly reactive in an oxidizing environment and must have a protective coating to insure its survival in a reentry environment. One potentially useful method of protecting these materials involves coating the surface with a polymer which is subsequently pyrolyzed to form an inert inorganic surface layer. Several polymers have been tested in an effort to produce an inert surface layer. It has been found that, under the pyrolysis conditions used so far, the surface layer contains a large amount of siliconoxycarbide (SiCO). It is important to determine the composition of this pyrolysis product and then to correlate it with coating preparation procedures in order to develop more effective protective layers.

Several experimental methods have been used to examine the changes in composition of the polymer under different pyrolyzing conditions. These include Infrared (IR) spectroscopy, thermogravimetric analysis and Inductively Coupled Plasma (ICP)

emission spectroscopy. The ICP provides the most quantitative compositional data on these and other materials containing boron, silicon, aluminum, and zirconium. However, samples to be analyzed with the ICP- Atomic Emission spectroscopy (AES) must be dissolved into a solution. Many of the newly developed materials containing carbides and borides are very resistant to traditional methods of dissolution, so new approaches, such as alkali carbonate flux dissolutions, are being investigated.

Carbonate Flux Dissolution of Carbides

In order to bring the SiCO into solution using mineral acids, it must first be fused with an alkali carbonate at high temperature. Unfortunately, the use of such a method often results in material losses that will taint the end analysis. It was discovered through experimentation that overall there are four controlled variables which determine the "method quality *". These variables are fusion material, fusion temperature, fusion duration, and sample to fusion material ratio.

It was originally believed that the high temperature required for fusion was responsible for material losses due to the increased volatility of most substances at high temperature. The use of a binary mixture of carbonates with a low melting eutectic was therefore tested in an attempt to minimize such losses. The method used potassium and sodium carbonate in a 1:1 molar ratio (eutectic melting point of 710°C) at a fusion temperature of 800°C. Fusion times and sample ratios were varied. The use of this method on pure silicon carbide produced errors ranging from ten to twenty percent. The source of this error is yet to be determined.

The use of sodium carbonate (m.p. 854°C) by itself as a fusion material proved to be more promising. Spot checks produced errors ranging from five to ten percent. Subsequently, the method was fine tuned in the following manner:

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* Method quality is defined as the percent recovery of the element being analyzed.

In order to determine optimum temperature, fusions were performed at temperatures ranging from 875°C to 1000°C, holding other variables fairly constant. The results showed that lower temperatures gave higher quality, most likely due to volatilization of components during fusion. Thus, all subsequent fusions were performed at 875°C.

Further experiments were run in order to pinpoint the ratio and duration that would produce the highest quality. Fusions were performed using a shotgun approach since it was not known which sample to fusion material ratio would yield the best results. A small representative set of the obtained data is presented in Table 1.

Table 1: Small data set from experimentation

Sample mass (g)	Fusion material mass (g)	Ratio	Time (min.)	Quality
.0329	1.0486	31.9	40	102%
.0273	1.0093	37.0	60	75%
.0260	1.0179	39.15	80	52%
.0314	1.0005	31.9	30	100%
.0264	1.0135	38.4	40	84%

Examination of the data suggests that a ratio of about 0.03 g of sample mass to 1.0 g of a fusion material in a duration of 30 to 40 minutes would consistently produce quality ranging from 98% to 102%. Follow up fusion runs confirmed this hypothesis.

Results of Oxidation Resistance Tests

The Scanning Electron Microscope (SEM) has been utilized to support research of high temperature carbon materials. Carbon tiles and felts were coated with various materials to protect the carbon from oxidation under extreme conditions. The SEM with an energy dispersive x-ray analysis unit attached was employed to investigate the different phases present in the specimens which led to the determination of whether the carbon was

oxidized or not. To date, the carbon fibers have oxidized in all cases, and the research effort continues.

(2) Ultra High Temperature Ceramics (UHTC)

The materials development effort has focused on advanced UHTC materials that are borides and carbides of the group IV metals, capable of withstanding temperatures up to 3000°C in an aeroheating environment. These UHTC materials will allow development of new types of leading edges for hypersonic vehicles, allowing a sharper reentry trajectory.

Arc jet testing of several variations of materials was recently completed in the Aero Heating Facility (AHF) at Ames. The goal was to produce a material that had an oxidation layer that was thin, dense, and adherent. In order to accomplish this, samples needed analyses before and after arc jet testing in order to investigate material performance in aeroheating environments. The samples involved in this series of testing were 0.75" in diameter and 0.25" thick. Some of the specimens had a small hole bored, by Electric Discharge Machining (EDM), in the back-face that came within 1/32 of an inch from the front surface. A fiber optic sensor, mounted inside the model assembly, protruded into this hole and was used to measure an in-depth temperature. Other sensors were used to make temperature measurements on the front surface of the specimen. The temperature differential across the thin oxide layer could then be determined by comparing the two measurements. The fiber optic sensor was also used to measure the back-face temperatures of specimens without in-depth holes. On the average, the oxide layers measured about 400 μm thick and had as much as a 300° C temperature drop across them. The measurements of the back-face temperature showed a 500-700° C temperature drop across the full 0.25" thick sample. Samples were analyzed using materialography, X-Ray Diffraction (XRD) analysis, SEM, Energy Dispersive X-Ray (EDX), IR, as well as other techniques. The

ICP was also used to analyze unknown coatings formed on the arc jet model holders during testing. The analysis showed that the coatings were the result of out-gassing by one of the constituents of the sample. In addition, materialography techniques had to be developed to analyze the microstructure of the pre- and post-test arc jet samples. An optical microscope was used to analyze the steps in developing materialographic techniques. Upon completion of sample preparation, the microscope was used to obtain a photographic image for reviewing and studying. Analysis of the microstructure showed that during processing, agglomerations formed between fine grained particles. These agglomerations caused highly porous regions that initiated failure and caused poor ablation performance. Therefore, work needs to be concentrated on improving the processing of these materials.

XRD analysis provided useful information in two areas. First, standard diffraction patterns were taken of each sample prior to testing to check for impurities and unexpected phase transformations that may have been produced in the processing stage. It was found that no new phases formed during processing and that impurities were negligible. Second, back-surface stress analysis of post-test samples was completed. To do this test, a different X-Ray tube had to be installed in the XRD. This required full readjustment and calibration of the machine. A powder sample containing the same material combination as the arc jet samples was analyzed to determine the baseline stress (A powder sample should have a surface that is relatively stress free). After this analysis was completed, pre- and post-test samples were placed in the XRD to measure the back-surface stress due to arc jet testing. It was found that the back face of the post-test samples were in compression unexpectedly. XRD diffraction patterns were also taken on selected post-test samples to analyze the change in surface chemistry due to the formation of the oxidation layer. In the future, all test surfaces will be analyzed for determination of materials present before and after testing.

Flexural testing and analysis of UHTC materials, using four-point bending in accordance with MIL Standard 1942, were also completed. The relative strengths pertaining to different combinations of ZrB_2, ZrC, and SiC were evaluated. The relative strength of HfB_2/SiC was also examined. Pre-test analysis performed on each sample consisted of bulk density, and weight loss/gain measurements along with sonic modulus testing. The sonic modulus is used as a non-destructive technique to estimate Young's Modulus. It involves measuring the natural frequency of the material when it is tapped and converting that into a modulus via an equation that relates the frequency to sample dimension and other material properties. Flexural testing was performed using a computer controlled Instron 1122 testing machine. Data received from the Instron's computer are in a form that is not easily transferable to other computer platforms, so macros were written in an EXCEL spreadsheet to analyze the data. These macros are adaptable to future testing programs. Post-test analysis also involved doing materialography on specimens after fracture. A correlation between strength, SiC agglomerations, and density was developed. From comparing micrographs to average strength, average density and SiC agglomeration formations, it was concluded that while additions of SiC helped to increase the average density and strength, porous agglomerations of SiC limited the strengths possible. It is known that a properly processed ZrB_2/SiC material can exhibit strengths on the order of 140 ksi. In this group of specimens the highest individual strength recorded was 108 ksi, but a high standard of deviation in strengths brought the average down to 45 ksi. This is attributed to a high quantity of SiC agglomerations that were formed during processing. However, these flexural bars were machined out of a scrap section of the pressing billet and are presumed to be a worst case scenario. The conclusion from flexural and Arc-Jet testing is that further work needs to be concentrated on the processing of these materials to improve the uniformity of the specimens and reduce SiC agglomerations.

A new all graphite model holder, coated with SiC for reusability, has also been designed for the next series of arc-jet testing. The purpose of the upcoming experiment is

to measure the catalyticity of UHTC materials. The specimen size has been changed to 3" in diameter and 0.125" thickness. Holes will be bored into the sample that come within 1/16 of an inch from the front-face of the sample. More locations for fiber optic sensors have been added with the increase in diameter of the specimen. A total of five sensors can be implemented at one time as opposed to only one in previous testing. This additional capability will allow in-depth and back-face temperatures to be collected simultaneously. Testing is currently in progress and is expected to be completed within the next year.